Indian J. Phys. **71A** (6), 651–656 (1997)

IJP A
— an international journal

Gamma-irradiation effect on dielectric properties of vanadate doped polyvinyl alcohol

M S Abo-Elil, M A Ahmed and M A El-Ahdal*
Department of Physics, Faculty of Science, Cairo University, Giza, Egypt
*National Center for Radiation Research and Technology, Cairo, Egypt

Received 20 September 1996, accepted 22 July 1997

Abstract : The real part of the dielectric constant (ε') for different concentrations (1%, 2% and 3% by wt) of the ammonium meta vanadate doped polyvinyl alcohol was measured as a function of temperature and frequency. Different γ-ray doses (2.0, 5.0 and 10 kGy) were used for samples irradiation. The dielectric constant of the samples reveals more than one peak depending on the vanadate concentration as well as the applied frequency. The main relaxation peak was discussed with reference degradation and crosslinking that vary drastically with the γ-dose. The hump that appeared at high temperature was found to be due to order-disorder transition The variation of the internal dynamic viscosity of the sample by irradiation was found to play a role in the polarization process as well as (ε') values. Gradual increase in (ε') was obtained by increasing the γ-dose.

Keywords : Dielectric properties, vanadate doped polyvinyl alcohol, gamma-irradiation effect.

PACS Nos. : 77.84.Jd, 61.82.Pv

1. Introduction

The interaction of radiation with polymers causes crosslinkage, degradation, gas evolution, unsaturation and colour formation [1]. Radiation-induced crosslinking of polymers is the most well known process in the field of industrial use of radiation. Due to large change in the physical properties of polymers by irradiation using moderate doses [2–5], γ-irradiation is used to change polymer properties. In most polymers, both crosslinkage and degradation take place.

It was found by Tabata [6] that the crosslinked polymer has a higher melting point than the normal one. Also the crosslinked polymer dissolved partially depending on the radiation dose. So the radiation can be used to improve the mechanical, chemical and

physical properties of polymer. Radiation causes ionization, excitation or radical production on one molecule which is attracted and combined with an adjacent polymer molecule not affected by radiation.

It is also assumed that radicals formed by irradiation are continuously mobile and can wander through an irradiated polymer until they meet up in pairs to from a crosslink. The result of radicals formation increases the molecular weight of the polymer until a three dimensional net work is formed. The only case in which the molecular weight decreases is that of predominating scission in the irradiated polymer.

There are many industrial applications for the cross-linking that are formed in polymers such as improving polymeric insulation on wires and cables, obtaining a better foam control, and improving plastic memory. The existence of a single hydroxyl group in polyvinyl alcohol using γ-rays, makes it very easy to change the polarization mechanism either in pure or doped samples.

2. Experimental

The polyvinyl alcohol and ammonium meta vanadate were in Analar grade from (BDH). The chemicals were dissolved in triply distilled water with different vanadate concentrations (1, 2 and 3%) by weight. The solution was poured in petri-dish and inserted in levelled furnace at 40°C. Complete drying were carried out to prevent fungi formation. The obtained film was cut to different parts and irradiated with different γ-doses of 2, 5 and 10 kGy using Co^{60}. Silver paste was used to cover the two surfaces of each sample and checked for good conduction. The dielectric constant was measured at different frequencies (1, 10 and 100 kHz) using a self-calibrated and computerized RLC bridge model (SR 720). The temperature of the samples was measured using k-type thermocouple (connected to Digi. sense (USA) thermometer) with junction in contact with the sample to avoid any temperature gradient. The accuracy of measuring the temperature was better than $\pm$ 1°C.

3. Results and discussion

Figure 1 is a typical curve that correlates the real part of dielectric constant (ε') and absolute temperature for polyvinyl alcohol doped with 2% weight of vanadate and irradiated with a γ-dose of 2 kGy. The data were collected at different frequencies of (1, 10 and 100 kHz). From the figure it is clear that ε' increases with increasing temperature until it reaches a maximum (relaxation peak) at $\cong$ 320 K, which shifts slightly with frequency. The effect of frequency on ε' appears as a general feature of Figure 1 in which ε' decreases with increasing frequency. At low frequency, the dipoles of the main chain of polyvinyl alcohol and those with vanadate, have the ability to follow up the field variation and increase the polarizability as well as (ε'). On increasing the frequency of the applied field, the dipoles are not able to follow up the field variation [7], thus a decrease in ε'.

values and a broadening of their peaks are obtained. The broad humps which appear after the glass transition temperature are expected to be due to the order-disorder transition of polyvinyl alcohol and its vanadate samples. The loss of the multiple hydrogen bounded water molecules as well as the single hydrogen one, could be responsible for the high dispersion process (high ε'). The sharpness of ε' which increases with decreasing frequency for different samples, may be due to either the formation of a boundary layer of blocked ions at the electrode surface [8,9] or Maxwell-Wagner type polarization [10,11]. Above the glass transition, the motion of the segmental parts is possible, also the macro-Brownian motion [12] of the segmental parts in the sample chains play a significant role in the polarization process.

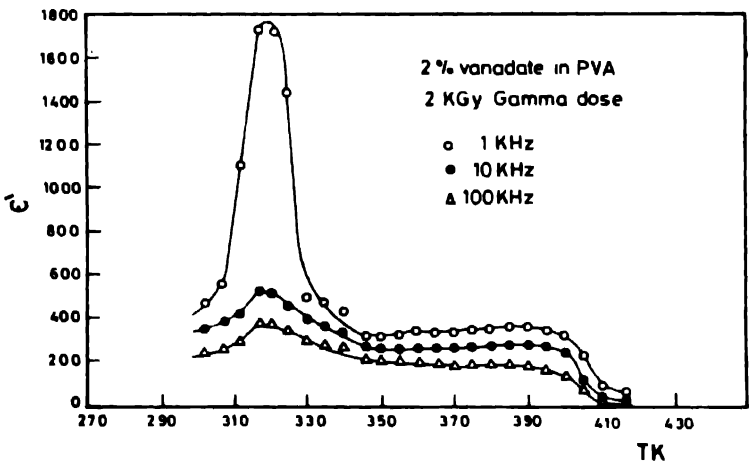

Figure 1. Relation between the real part of the dielectric constant (ε') and absolute temperature for polyvinyl alcohol doped with 2% weight of vanadate and irradiated with a γ-dose of 2 kGy at different frequencies.

Figure 2 correlates the real part of the dielectric constant (ε') and absolute temperature at frequency of 10 kHz for pure and doped samples with different vanadate concentration (1%, 2% and 3% by weight). All samples in Figure 2 are irradiated at 2 kGy. The data shows an increase of ε'_{max} with increasing vanadate concentration at the same γ-dose of 2 kGy. A broad hump (step transition) at ≈325 K begins to appear for 1% vanadate at frequency of 10 kHz. The position of the hump shifts to lower temperature by increasing vanadate concentration at the same γ-dose (2 kGy). The relaxation peak which appears at ≡ 337 K in pure polyvinyl alcohol shifts to the lower value ≡ 327 K for 3% vanadate. Between the relaxation peak and the hump for 2% vanadate a nearly stable value of (ε') is obtained. The half peak width of the 2% vanadate is greater than any of the other concentrations. This peculiar behaviour enhances the suggestion that 2% is the critical concentration in the present work. A closer look at Figure 2 indicates that ε' of the 3% vanadate begins to increase after reaching a minimum at about 340 K. This means that the

polarizability of the system is increased after this temperature due to the effect of the field accompanying the applied frequency which aligns more dipoles after this temperature. In other words, at 3% vanadate the thermal energy given to the system above 340 K liberates more frozen dipoles and the chance for the field to align them increases.

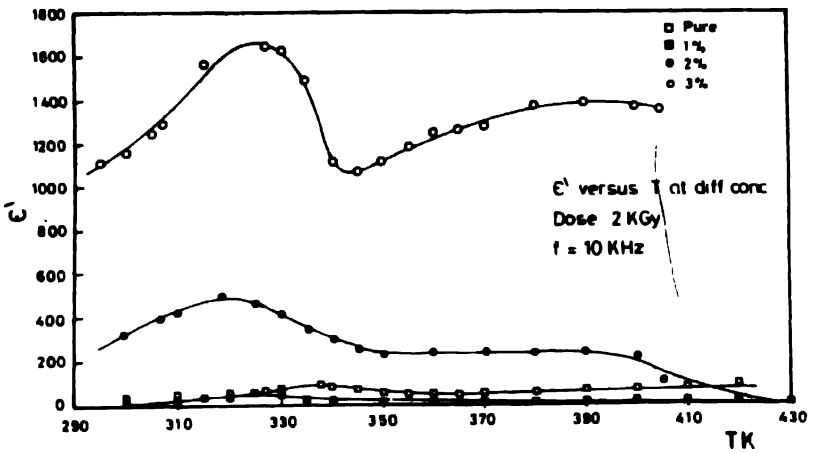

Figure 2. Relation between the real part of the dielectric constant (ε') and absolute temperature at frequency of 10 kHz for pure and doped samples with different vanadate concentrations (1%, 2% and 3% by wt.).

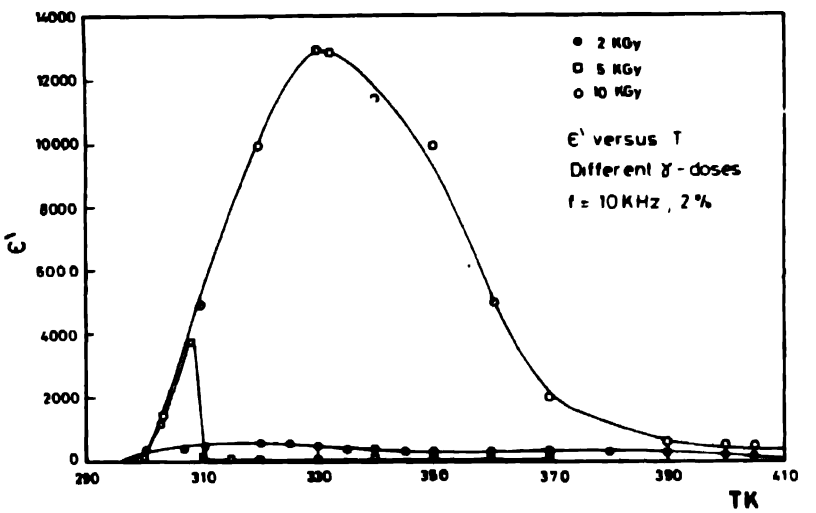

Figure 3. Relation between the real part of the dielectric constant (ε') and absolute temperature as a function of the γ-dose at frequency of 10 kHz for polyvinyl alcohol doped with 2% weight of vanadate.

The variation of ε' with the absolute temperature as a function of γ-dose is shown in Figure 3. The effect of γ-dose can be considered as to increase the interfacial (Maxwell-

Wagner) polarization at the segmental parts. The degradation that is caused by γ-rays will initiate more mobile segments which help in the polarization process leading to an increase in ε'. From the Figure, it is also observed that the main relaxation peak has been shifted from 315 K to 305 K by increasing the dose from 2 kGy to 5 kGy and returns back to higher temperature (335 K) at 10 kGy. This may be attributed to the more thermal energy needed to overcome the effect of internal relaxation of the oriented dipoles at 10 kGy and an increase in the crosslinking which competes with the degradation due to irradiation with such higher dose, may take place. The shift in the relaxation peak to lower temperature can be ascribed to the generation of low-molecular weight species and free chain ends with irradiation [13]. The interaction of Compton scattered electrons with the bonds may be considered as the direct effect of the interaction of the gamma-rays with sample to form another free radicals and carbon monoxide *via* Norrish reaction [14]. This means that the free redicals formed by γ-rays, are mobile and can wander through the irradiated polyvinyl alcohol, pure and doped with vanadate of different concentrations, until they meet up in pairs to form crosslink. Also the γ-irradiation will cause the loss of hydrogen (radical) atom which abstracts another hydrogen atom from neighbouring molecules and the two free radicals may crosslink.

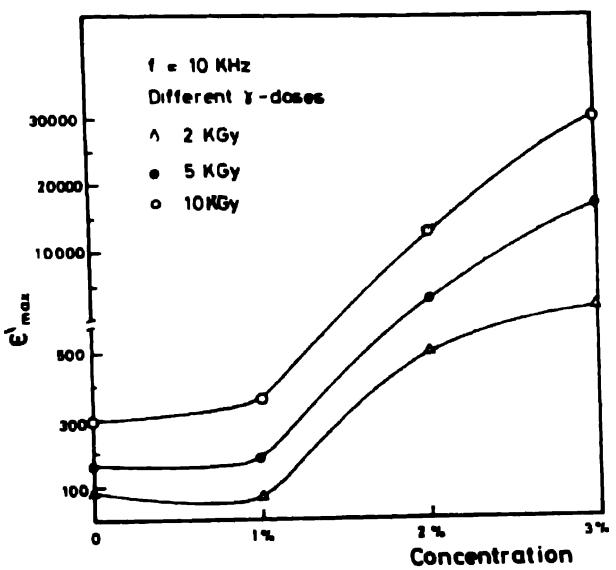

Figure 4. Variation of ε'_{max} with concentration as a function of γ-dose at frequency of 10 kHz.

The variation of ε'_{max} with concentration as a function of γ-dose irradiation is shown in Figure 4. As it was expected previously, ε'_{max} increases with increasing vanadate concentration and γ-doses. The increase of ε'_{max} with concentration is due to the increase of charge carriers as well as the crystallinity in the system, while the

increase in ε'_{max} with γ-dose is due to the increase of the segmental parts produced by degradation.

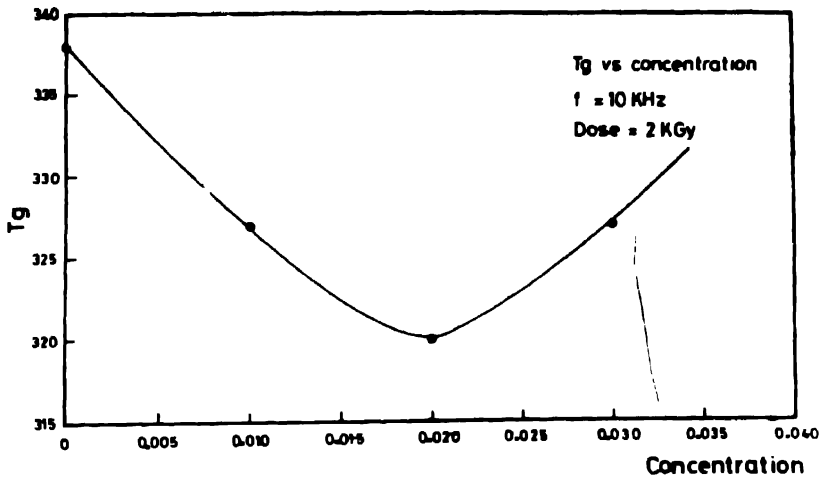

Figure 5. Relation between the glass transition temperature (T_g) and concentration at a γ-dose of 2 kGy and applied frequency of 10 kHz

Figure 5 correlates the glass transition temperature (T_g) with concentration at a γ-dose of 2 kGy and applied frequency of 10 kHz. From the figure, T_g reveals a decrease with increasing concentration up to 2% wt after which it increases again. This results agree well with the suggested critical concentration of 2%.

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